Study on Anneal Hardening of Copper Alloys

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I. Introduction

A phenomenon similar to strain age hardening of steel can be observed in copper alloys, and it is called "anneal hardening".

The study of its fundamental principle has been made by different workers, and led to many theories,[1][2] by which it seems to be difficult to account satisfactorily for the fact that when heavily extended brass is annealed at temperature ranges of anneal hardening, the yield point measured by the same stress as prior tension is not raised but rather lowered,[3] in spite of showing increase in hardness, while when a specimen of the same material is cold rolled, the yield point rises. Therefore, it may be necessary for the study of anneal hardening to clear the effect of conditions of cold work.

α brass shows marked anisotropy in Young's modulus[4] and deformation resistance,[5] on the other hand, Al, which does scarcely present anneal hardening, shows only a slight anisotropy in Young's modulus. Thus, the seemingly contradictory relation between the lowering of yield point and anneal hardening above mentioned, may be due to a marked anisotropy in strength.

It has been already reported that in steel, there were remarkable effects of mode and direction of cold work on strain age hardening,[6][7] while in copper alloys, these effects on anneal hardening have not yet been specifically investigated, although some pertinent observations have been made.

The present investigation has been carried out on some copper alloys to study the relations above mentioned and furthermore the nature of anneal hardening.

II. Dilatometric Measurements

Specimens used in the measurements were prepared by melting electrolytic copper, zinc free from arsenic and 99.8% aluminium in graphite cruicible. The measurement was done with Honda's differential dilatometer, by which the difference between the dilatometric changes of the specimen to be studied and a reference specimen of the same alloy in unworked state, was recorded. Heating rate during measurements was about 1.8°C/min..

1. *Effect of Condition of Cold Work*

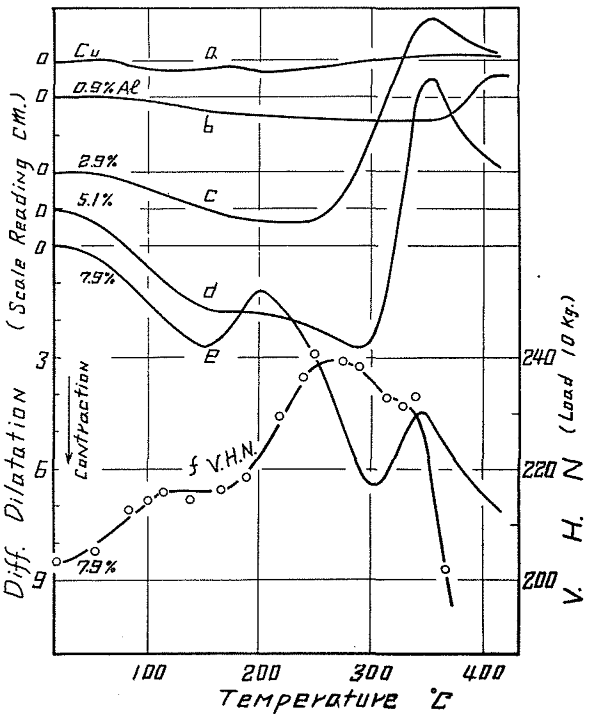


Fig.1 Thermal dilatation and hardness curves for 64% drawn specimens of Cu-Al alloys.

Fig. 1 shows thermal dilatation curves of 64% drawn specimens of various Cu-Al alloys. Al content of the alloys is indicated near the curves. Amount of the changes increases with Al content. Curve (f) shows the relatiion of annealing temperature and hardness of 7.9%Al-Cu alloy. Here, annealing of specimens for measurement of hardness was performed by heating up to the temperature indicated on the abscissa at a rate of about 1.8°C/min. and then air cooling. In all the experiments here-under, annealing was made under such conditions, unless indicated otherwise. Increase in hardness shown by curve (f) occurs in two stages, respectively corresponding to the primary and the secondary changes of contraction (curve e).

Fig. 2 shows thermal dilatation curves of drawn specimens of *α* brass. Amount of various changes, especially, of the secondary contraction (130-250°C) and the secondary expansion (250-280°C), increases very markedly when the reduction of drawing is more than about 25%. As was the case with 7.9% Al-Cu alloy in Fig.1, anneal hardening was also observable in

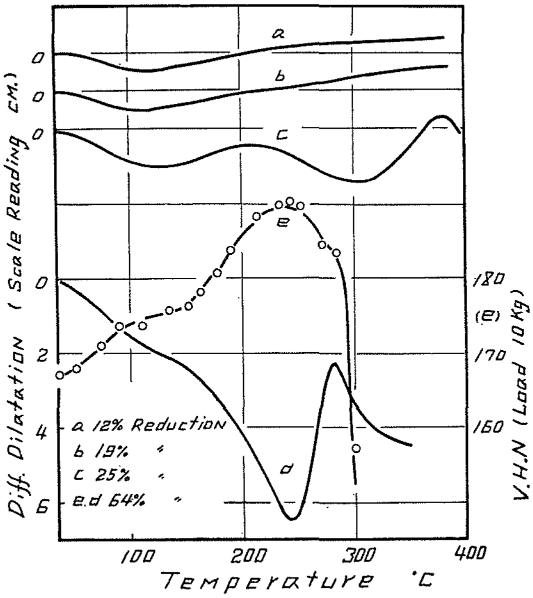


Fig. 2 Thermal dilatation curves for 28.4% Zn-Cu alloy drawn to various reductions.

brass in the temperature ranges of the contractions (curve e).

Such complicated changes in dilatation show dissimilarity with different modes of cold work.

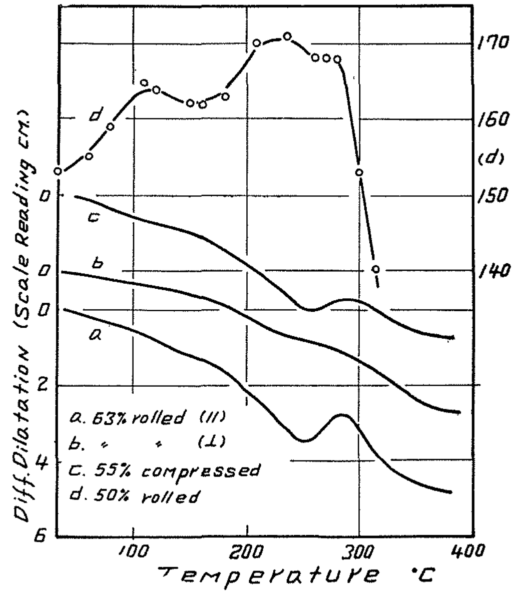


Fig.3 Thermal dilatation curves for rolled and compressed specimens of 28.4% Zn-Cu alloy.

Fig.3 shows the changes in dilatation and hardness of rolled and compressed specimens of α brass. Curve (c) concerns a specimen compressed perpendicular to its axis, and curves (a) and (b) specimens rolled in the directions parallel and perpendicular to their axis, respectively. Amount of the change is smaller in any case. The change in dilatation is different in different rolling directions, and besides shows no conformity with that in hardnees shown by curve (d).

Further attempts were made by tension. The change is rather simple, as shown in Fig.4. Hence, it is evident that the change in dilatation differs widely with the modes of cold work, but the change in hardness, which is measured without reference to direction, is not much affected by the mode.

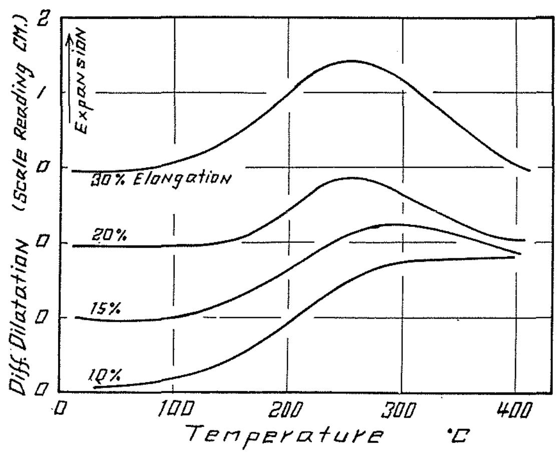


Fig.4 Thermal dilatation curves for 28.4% Zn-Cu alloy elongated in various degrees.

2. *Change in Density*

The most likely cause of the dilatation changes was thought to be mainly a directional change. To verify this, density measurements were made. The mothod of determining density is based essentially upon measuring the volume of the water being identical to that of specimen. Low temperature annealing was performed by heating at a rate of about 1.8°C/min. up to the temperature illustrated on the abscissa in

Fig.5 and then air cooling.

By curve (a) in Fig.5 is shown the change of density due to low temperature annealing of 64% drawn specimens of α brass, wherein it is evident that the change in density is very slight in the range below 200°C. The other curve (b) in the same figure shows the change in density of the same specimen, calculated on the assumption that the change in thermal dilatation, shown by curve (d) in Fig. 2, is isotropic. These calculated values are much larger than the measured.

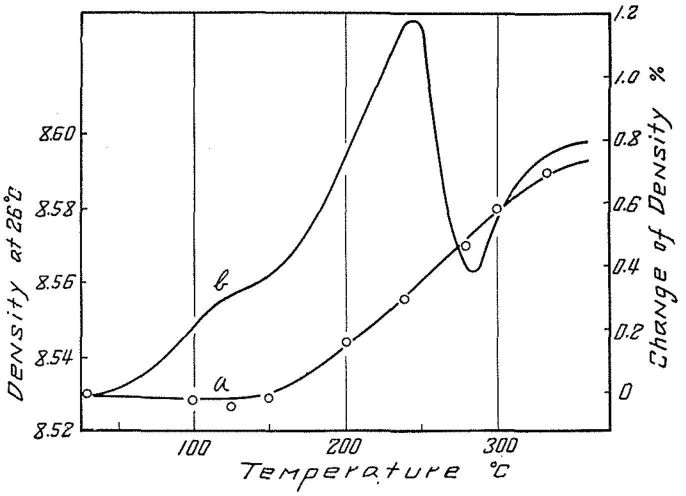


Fig.5 Change of density of 64% drawn specimens of 28.4% Zn-Cu alloy.

Therefore, the changes in thermal dilatation are confirmed to be directional. However, a very slight increase in the density can be observed in the temperature range of the secondary contraction (130-250 °C), in which an isotropic contraction seems to occur simultaneously.

A similar change is observed also in carbon steel. A change of expansion, as shown by curves (a), (b) and (c) in Fig.6, occurs in the temperature ranges of hardening (curves d and e). This change is also directional.[7]

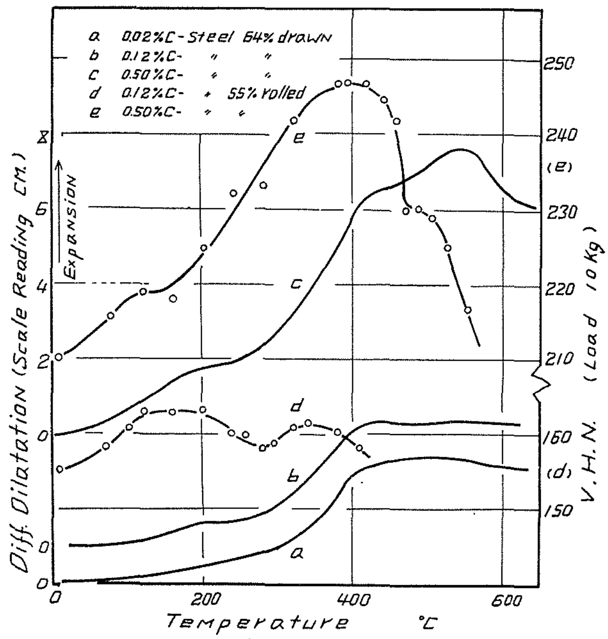


Fig.6 Thermal dilatation and hardness curves of carbon steel.

3. *Relaxation of Macro-Stress*

Since the change in thermal dilatation above mentioned, is considered to seemingly be due to a relaxation of macro-stress, the relaxation process was

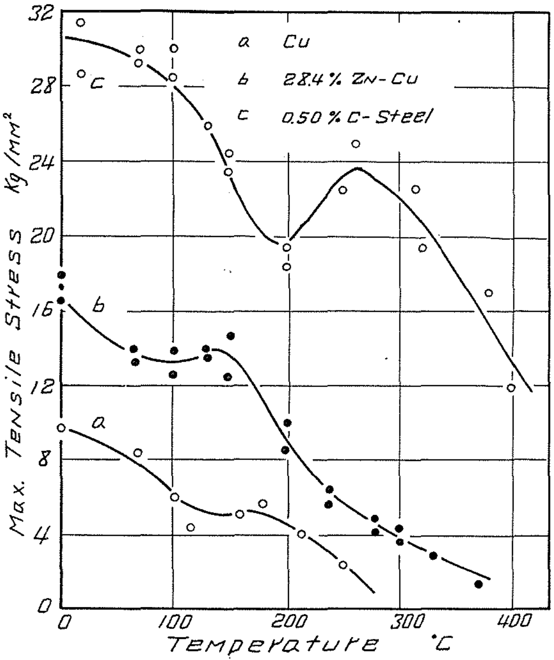
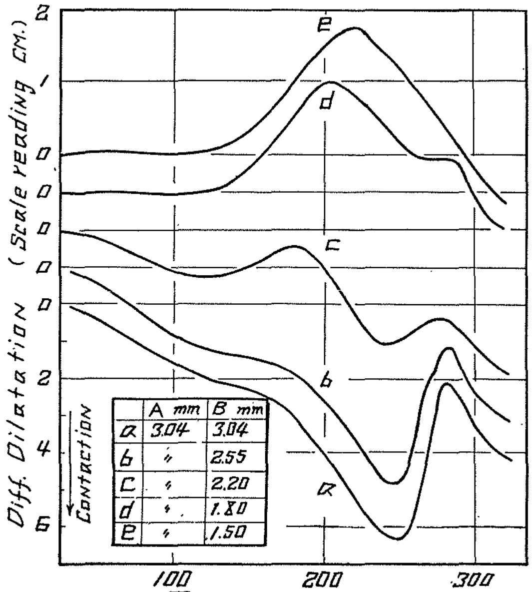


Fig.7 Change of macro-stress by annealing of 64% drawn specimens of Cu and some alloys.

studied. Hyne's method was adopted for measurement of residual stress. The specimen was immersed in mixed solution of hydrochloric and nitric acids for dissolving away the outer layer of specimen, and the change of length in the direction of specimen axis was measured to calculate the residual stress thereby. The method of low temperature annealing was the same as that in the case of density measurements above mentioned. As the results, it was found that a tensile stress distributed in the outer layer and a compressive stress in the central layer of the drawn specimens.

Curve (b) in Fig.7 shows the relaxation process of macro-stresses of 64% drawn specimens of α brass. The ordinate in the figure shows the maximum value of the tensile stresses distributed in the outer layer of specimen. The residual stress relaxes in two stages, the release being particularly marked in the temperature ranges of anneal hardening.

Such a relaxation can also be observed in pure copper (curve a), which shows only a very small change in thermal dilatation as shown by curve (a) in Fig. 1. This is of importance, since it is presumed that the above mentioned change in the



	A mm	B mm
a	3.04	3.04
b	〃	2.55
c	〃	2.20
d	〃	1.80
e	〃	1.50

Fig.8 Thermal dilatation curves for 28.4% Zn-Cu alloy specimens 64% drawn and dissolved to various diameters in acid.
A : Diameter of drawn specimen.
B : Diameter after dissolution.

thermal dilatation is not merely dependent on the relaxation of macro- stress.

Further attempts were made for the confirmation of the above stated presumption. Thermal dilatation curves shown in Fig. 8 were obtained by measurements on 64% drawn specimens of α brass eroded with aquaregia as in the test on macro-stress, and reduced to different diameters.

The thermal dilatation of the central layer of drawn specimens, as shown by curves (d) and (e), shows nearly the same tendency as that in extended specimens (Fig.4), suggesting that the central layer exhibits a tension structure, and furthermore that the contractions in the temperature ranges of anneal hardening of drawn specimen, occur only at its surface layer. It may be considered from the above observations that the complicated changes in thermal dilatation previousiy stated, is not caused by relaxation of macrostress but by a change in internal structure, in which vacancies and dislocations exhibit an anisotropic distribution depending on the condition of cold work, as Calnan reported.[8] The change in thermal dilatation may, therefore, be attributed to diffusion of the defects above mentioned.

4. *Room Temperature Ageing*

The primary contraction (below 140°C) observed in the dilatation curve of cold drawn α brass (curve d in Fig. 2), is found to become small after room temperature ageing, as revealed by curve (b) in Fig. 9. The contraction goes on rapidly immediately after drawing, similarly to the change in hardness shown by curve (a). A similar change occurs also in the recovery process of internal friction of cold worked α brass. The activation energy for the process is very small and substantially lower than 10,000 cal/mol,[9] suggesting that the various changes at room temperature are chiefly due to migration of pairs or aggregetes of vacancies. This will be described in chapt. V.

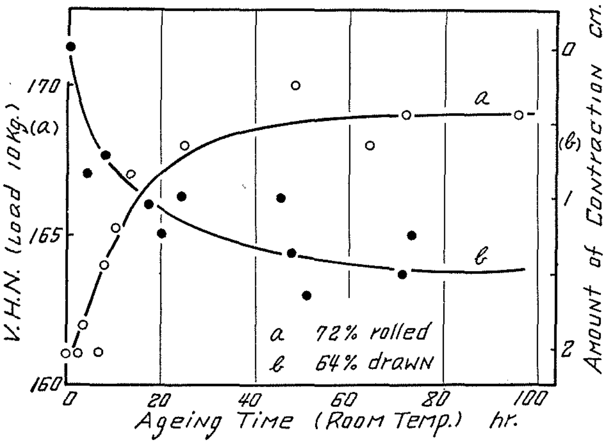


Fig.9 Change of the primary contraction (b) and hardness (a) of 28.4% Zn-Cu alloy during ageing at room temperature.

5. *Effect of the Secondary Working*

A deformation structure where lattice defects are non uniformly distributed, can be deranged not only by low temperature annealing, but by mechanical treatment. The experimental results on such a treatment, are shown in Eig. 10. The change in thermal dilatation of a specimen 64% drawn and subsequently 5% rolled, as shown by curve (b) is conspicuously different from that of as-drawn specimen (curve a), and a specimen secondarily rolled to 30% reduction shows a complete rolling structure (curve d).

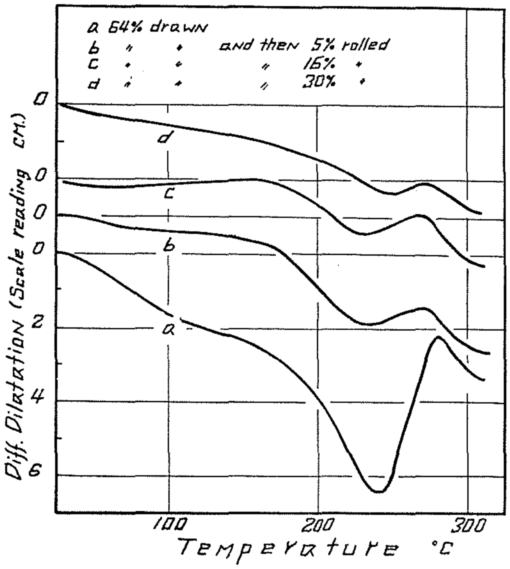


Fig. 10 Thermal dilatation curves for 28.4% Zn-Cu alloy 64% drawn, and subsequently rolled to various reductions.

As will be described in chapt. VI, a hardening similar to anneal hardeng can be observed by a slight application of the secondary working differing from the primary in mode, and therfore, the deformation structure above mentioned, is presumed to be closely related with anneal hardening.

6. *Retrogression Effect*

A study on the retrogression effect by dilatometry led to the results shown in Fig. 11. Dilatation curves on reheating after annealing at the temperature range (250-280°C) of the secondary expansion observed in a drawn specimen of brass (curve a in Fig. 10), show the secondary contraction and the secondary expansion again, which would be expected to be removed by prior annealing. Although these changes are not so larger as in the case when a specimen was heated directly after drawing, it may still be one of retrogression effects. This

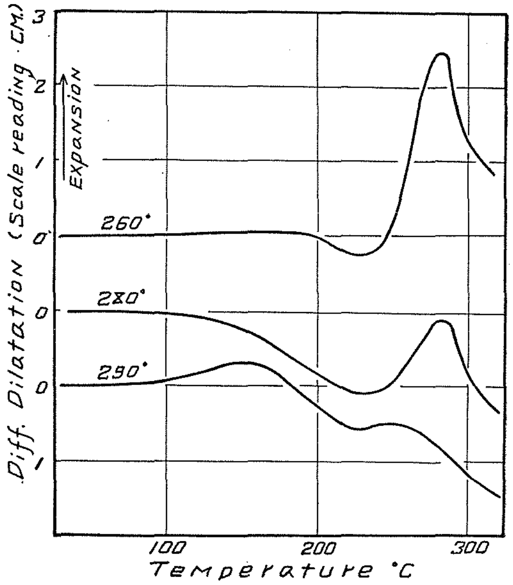


Fig.11 Thermal dilatation curves for 28.4% Zn-Cu alloy 64% drawn and heated to the illustrated temperatures.

effect, however, is not necessarily attributed to the same mechanism as observed in the case of age hardenable Al alloys. This will be described in chapt. VI.

7. *Conclusion*

The change in thermal dilatation of cold worked α brass and Cu-Al alloys was studied and the results obtained may be as follows:

(1) Amount of change in dilatation increases prominently when concentration of solute and degree of cold work increase beyond a certain limit, and also is greatly affected by the conditions of cold working.

(2) From the fact that the change in thermal dilatation of cold worked pure copper was very small compared with that of brass, in spite of presence of high residual stresses, it was ascertained that such a change in dilatation was not due to relaxation of macro-stress. It may be presumed that vacancies and dislocations exhibit an anisotropic distribution depending on the condition of cold work, and the diffusion of these defects causes abnormally large changes in thermal dilatation.

III. Thermoelectric Measurements

In chapt. II, it was presumed that the deformation structure of the copper alloys induced by cold work, was closely related to the anisotropy in arrangement of lattice defects. This relation in face centered cubic metals was studied by Calnan,[8] who pointed out that the anisotropy was weak in Cu and Al but very pronounced in α brass. Such an anisotropy is hard to detect by measurements of physical properties, such as electric resistance, but the process of recovery due to migration of lattice defects can be examined. In the following, the experiment on this subject was performed by measurements of thermo-E.M.F. with the aim of investigating the correlation between anneal hardening and recovery of physical properties of cold worked copper alloys. Although thermo-E. M. F. is rather complicated property, it is convenient for examining the effect of conditions of cold work, in particular, of the secondary working, on anneal hardening. On this basis, measurments of thermo-F.M.F. were carried out.

The method consisted in measuring thermo-E.M.F. of a couple formed by the drawn wire to be studied and a reference wire of the same alloy in unworked state. Thermo-E. M. F. between 0° and 60°C was measured directly by a sensitive galvanometer. Low temperature annealing of the wires was performed by immersion for 5 minutes in oil bath of the desired temperatures. Specimens were prepared by the same method as described in chapt. II.

1. *Effect of Degree of Cold Work*

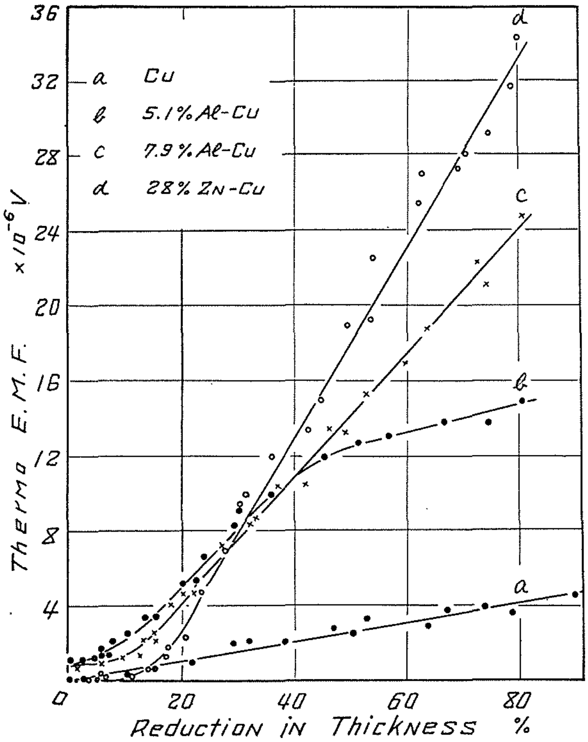


Fig.12 Relation between thermoelectric force (0°~60°) and rolling reduction of Cu and its several alloys.

The relation between thermo-E.M.F. and degree of cold rolling of pure copper and its alloys is given in Fig. 12. In copper, thermo-E. M. F. increases approximately linearly with degree of cold work, and the result is considered to well coincide with that of Brindley.[10] While in the other alloys, there may be a critical degree of cold rolling for the increase in thermo-E. M. F., which increases pronouncedly beyond 10% reduction. Such a critical degree of cold work can also be observed in the change in thermal dilatation already stated, in density[11][12] and in resistance to deformation,[13] suggesting that cross slip begins to occur at this range.

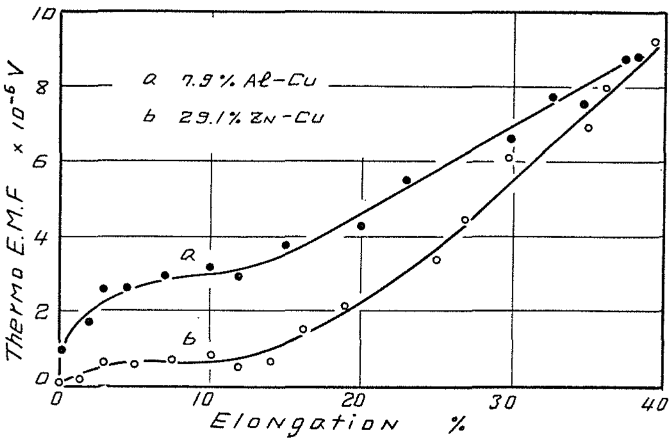
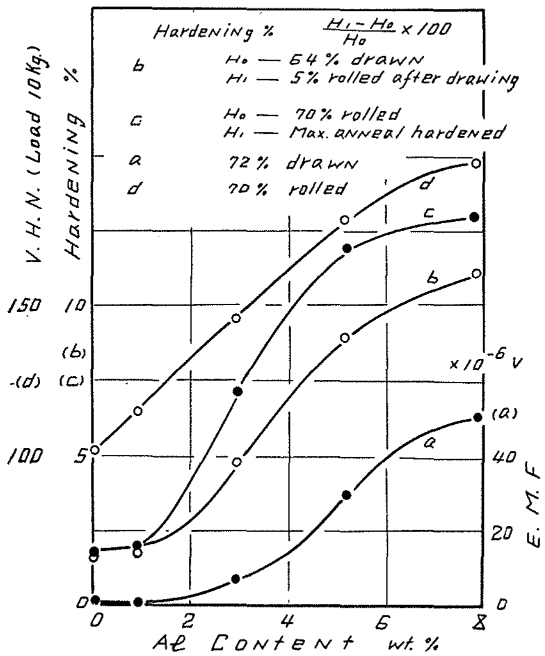


Fig.13 Relation between thermoelectric force (0°~60°) and elongation by tension of Cu-Al and Cu-Zn alloys.

In Fig.13 are shown the results of thermo-E. M. F. of extended specimens of copper alloys. The trend is similar to that shown in Fig.12.

As compared with rolling and extension, drawing induces much larger thermo-E. M. F.. Curve (a) in Fig.14 shows the relation between thermo-

E. M. F. and Al content of 72% drawn specimens of Cu-Al alloys. It may be cleared from the results that thermo-E.M.F. increases abruptly when Al content increases beyond about 2 wt%, and this tendency is nearly the same as that of change in electric resistance.[14]



Eig.14 Relation between Al content and various properties of cold worked Cu-Al alloys.

Increase in electric resistance due to cold work has been accepted chiefly as due to generation of vacancies, which are resulted from cross slip. and hence, it seems that a high enough concentration of solute is required for the occurence of cross slip beyond the critical degree of cold work. The effect of concentration of solute on anneal hardening shows a similar tendency (curve e in Fig. 14), suggesting that the vacancies constitute the cause of anneal hardening.

Similar attempts were made with carbon steel. The result is revealed by curve (a) in Fig. 15. Unlike in the copper alloys, in carbon steel thermo-E. M. F. increases steeply upon slight rolling, but upon severe rolling, the amount of increase is smaller. Such peculiarities of the increase in thermo-E. M. F. due to cold work in the copper alloys and carbon steel are in good correspondence with those of anneal hardening, respectively. This will be described later.

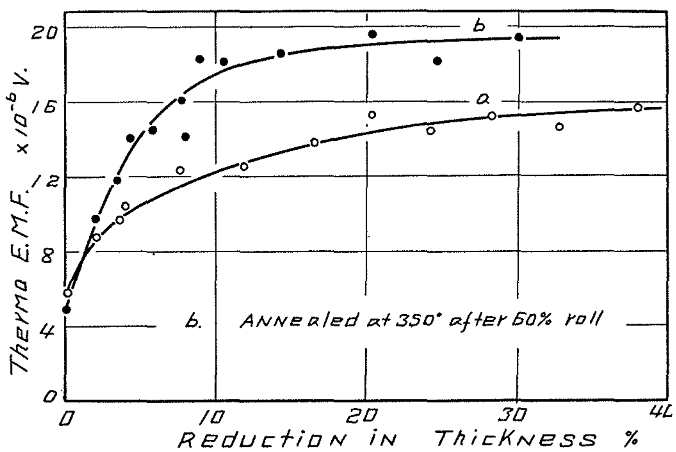


Fig.15 Relation between thermoelectric force (0°～60°) and rolling reduction of 0.5% C steel.

2. *Effect of Low Temperature Annealing*

Thermo-E. M. F. of cold worked specimens of α brass was found to change by annealing as shown by curves (a)~(d) in Fig. 16. Thermo-E.M.F. decreases in two stages within the temperature ranges of anneal hardening, respectively corresponding to the two stages of anneal hardening. This change is not so much affected as that in thermal dilatation by the mode of cold work.

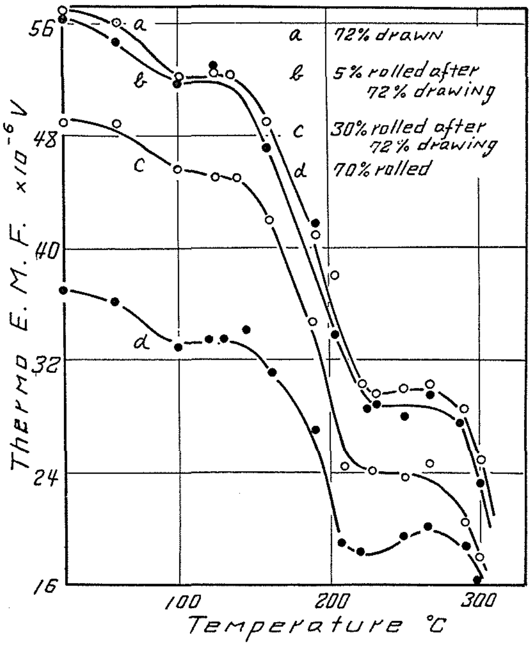


Fig.16 Change in thermoelectric force (0°~60°) with annealing temperature of 29.1% Zn-Cu alloy.

It may be relevant to mention from the above resuts that vacancies in various states disappear in three stages between room and recrystallization temperatures.

Also in carbon steel the same tendency is apparent, as shown by curve (a) in Fig. 17, with the exception that the effect of cold work is almost removed by annealing at about 300°C, that is, the change with reference to recrystallization is absent. Here, for low temperature annealing of carbon steel, both oil bath and Sn bath were used.

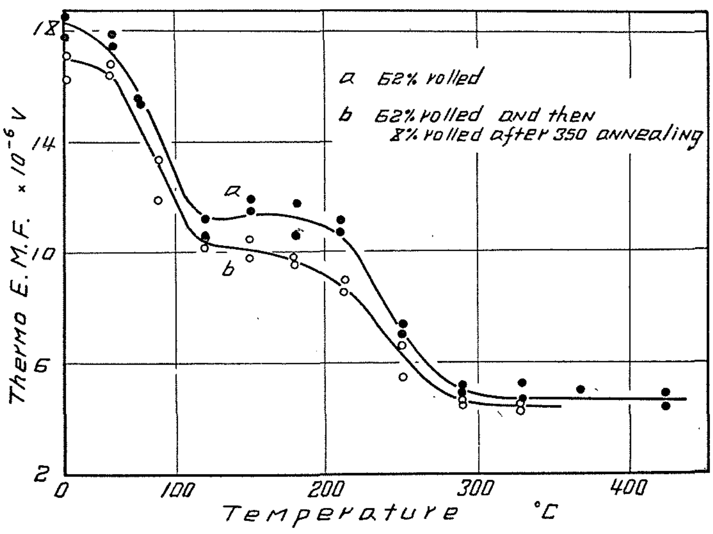


Fig.17 Change in thermoelectric force (0°~60°) with annealing temperature of 0.5% C-steel.

3. *Effect of the Secondary Working*

In Fig.18 is shown the relation of the degree of rolling versus thermo-E.M.F. of 72% drawn specimens of α brass. No special question arises when the primary and the secondary workings are of the same mode, but when they are different, it becomes rather complicated, namely, even when a specimen is secondarily rolled to about 10% reduction, scarcely any change appears in thermo-E.M.F., showing dissimilarity in this respect from the change in thermal dilatation.

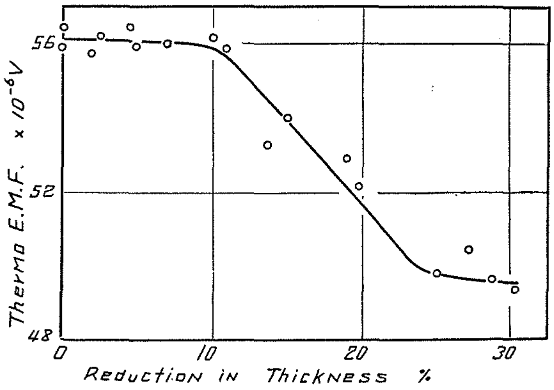


Fig.18 Relation between thermoelectric force (0°～60°) and rolling reduction of 21.9% Zn-Cu alloy previously 72% drawn.

As will be described later, a hardening of the same degree as anneal hardening is induced by a slight application of the secondary working. The fact that, in the range of degree of the secondary working at which this hardening takes place, any perceptible change in thermo-E. M. F. does not occur, shows that thermo-E. M. F. is considered not to show directionality, being different from the thermal dilatation and strength.

In Fig. 18, thermo-E. M. F. shows a sudden drop at about 10% reduction. Thermo-E. M, F. would be expected to increase with increasing degree of cold work, but on the contrary, it decreases here. In spite of absence of marked difference in the degree of work hardening at 60% reduction, thermo-E. M. F. was 37×10^{-6} V. after rolling and it is much smaller than the value 56×10^{-6} V. after drawing. It appears, therefore, that the anomalous drop of thermo-E.M,F. in Fig. 18 is due to the extinction of excess vacancies while the as-drawn structure transforms into the rolling structure. Such a difference in thermo-E. M. F. due to different modes of cold work is pronounced only in the alloys which show marked anneal hardening.

Fig. 19 reveals the effect of the secondary working of the same mode as the primary. Here, heavy rolling was applied first, then annealing was done at the temperatures indicated near the curves, and again rolling was applied to the degree illustrated on the abscissa. In any case, thermo-E. M. F. never return to the value before low temperature annealing (56×10^{-6}V.) by a slight application of the secondary rolling, and it is understood that the increase of thermo-E.M. F. corresponding to work softening[15] observed in anneal hardened material

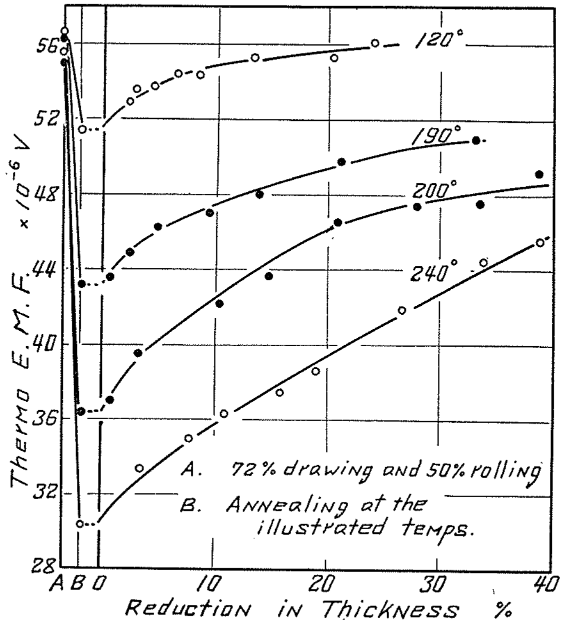


Fig.19 Relation between thermoelectric force (0°~60°) and rolling reduction of 29.1% Zn-Cu alloy after rolling and subsequent annealing at the illustrated temperatures.

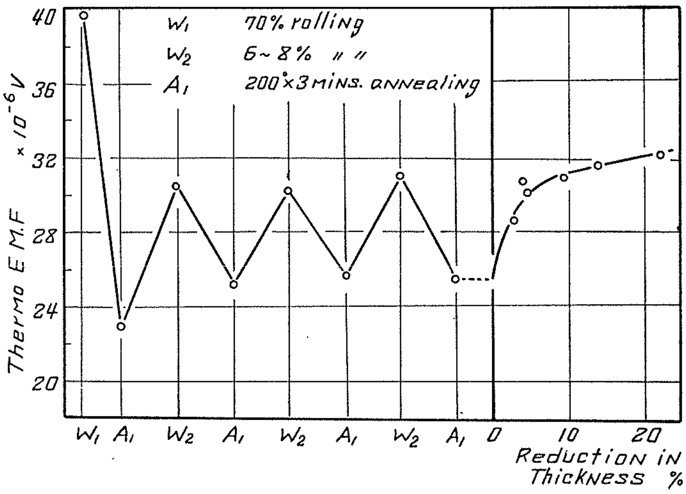


Fig.20 Effect of repeated slight rolling and annealing on thermoelectric force (0°~60°) of 29.1% Zn-Cu alloy previously 70% rolled.

(Fig. 38), is very small. As shown in Fig. 20, however, reversibility appears to some extent when annealing at 200°C and slight rolling are repeated.

The results obtained with carbon steel showed marked difference from those with brass. In carbon steel, thermo-E.M.F. comes back nearly to the value just after the primary rolling by an application of the secondary slight rolling after 350°C annealing, as shown by curve (b) in Fig. 15.

4. *Conclusion*

The results on measurements of thermo-E.M.F. of cold worked α brass and Cu-Al alloys led to the following conclusions:

(1) Thermo-E.M.F. of cold worked specimens depends closely on the mode of cold working. It may be presumed that number of vacancies generated during cold work, is widely different for different modes of cold work.

(2) Anisotropy in internal structure induced by cold work could not be detected by measurments of thermo-E. M. F., unlike in the case of thermal dilatation.

This property after cold work is considered to increase mainly by the formation of vacancies, and in addition, to scarcely depend on the anisotropy in arrangement of vacancies, but chiefly on their number. It is inferred from the experiments that vacancies are an important factor in anneal hardening.

(3) A high enough concentration of soute is required, in the copper alloys, for the easy occurence of cross slip, by which vacancies generate. In accordance, pure copper shows only a slight increase in thermo-E.M.F. by cold work.

Electric resistance is considered to be subjected to a similar change as thermo-E.M.F..

IV. Anelastic Effect

Bauschinger effect can be observed not only in the reverse direction but in all the directions except that of prior working.[16] It seems unaccptable to explain the effect by the mechanism that this effect is only due to residual stress, for thereby it may be impossible to explain why, in spite of the disappearance of this effect upon annealing within the temperature ranges of anneal hardening, the yield point in the working direction is not lowered.

The effect is very marked in brass,[16),17),18)] but weak in Al[16),19)] which shows little or no anneal hardening. It is the aim of this study to inquire into the relation between such an anelastic effect and anneal hardening.

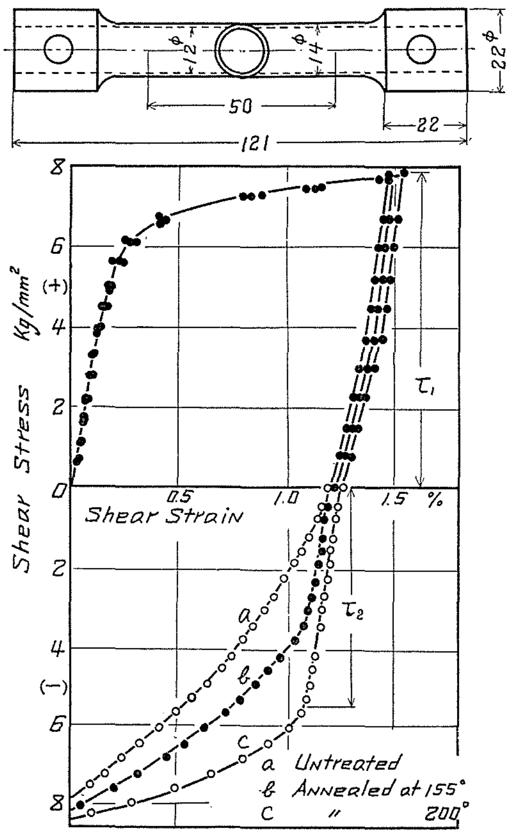
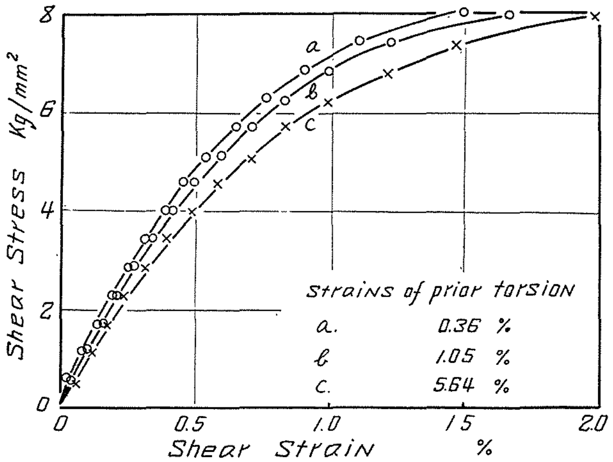


Fig.21 Torsion stress strain diagram of 33.2% Zn-Cu alloy annealed at zero stress.

Experiments on Bauschinger effect were carried out by torsion, which was adapted to a reversal of stress. The material used in this experiment was a commercial brass, and it was supplied in the form of thin walled hollow cylinders with the dimensions shown in Fig. 21, in order to homogenizing the distribution of applied stress. Specimens in the other experiments were prepared by the same method as described in chapt. II, and low temperature annealing was also made by the method of constant rate heating.

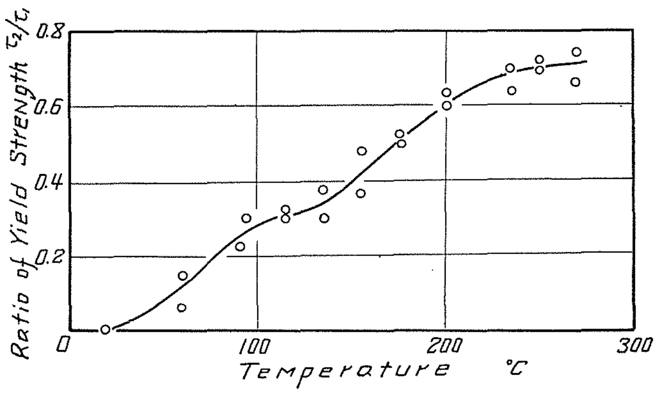
1. *Bauschinger Effect*

Specimens were first twisted followed by annealing under zero load at various temperatures, and then re-twisted in the direction reverse to the prior torsion. The results are given in Fig. 21. As shown by curve (a), which concerns a specimen without annealing before torsion to the reverse direction, brass shows a marked Bauschinger effect. Moreover, as shown in Fig. 22, the higher the degree of prior torsion, the more marked the effect.



Eig.22 Torsion stress strain curves of 33.2% Zn-Cu alloy upon reversed loading after primary torsion.

The yield point in the reverse direction is raised by low temperature annealing (curves b and c in Fig.21). Temperature dependency of the ratio τ_2/τ_1 is revealed in Fig.23. Here, τ_1 and τ_2 are noted in Fig.21. The ratio increases in two stages within the tempetature ranges of anneal hardening. This tendency is similar to that of increase in hardness (Fig.2) and decrease in thermo-E. M. F. (Fig.16).



Eig.23 Change in ratio τ_2/τ_1 of 33.2% Zn-Cu alloy with annealing temperature.

2. *Change of Yield Strength by Low Temperature Annealing*

Hardening would be expected to be accompanied by a rise in yield point, but in brass, the results contrary to this expectation were reported.[3] To verify this, measurements of yield point were performed by tension, for which Amsler's universal testing machine was employed.

Relation between change of yield point in the same direction as the primary tension and annealing temperature is given in Fig.24. In α brass (curve a), yield point shows little rise but rather lowers within the temperature ranges of anneal hardening (below 230°C). In Cu-Al alloy (curve b), it shows only a

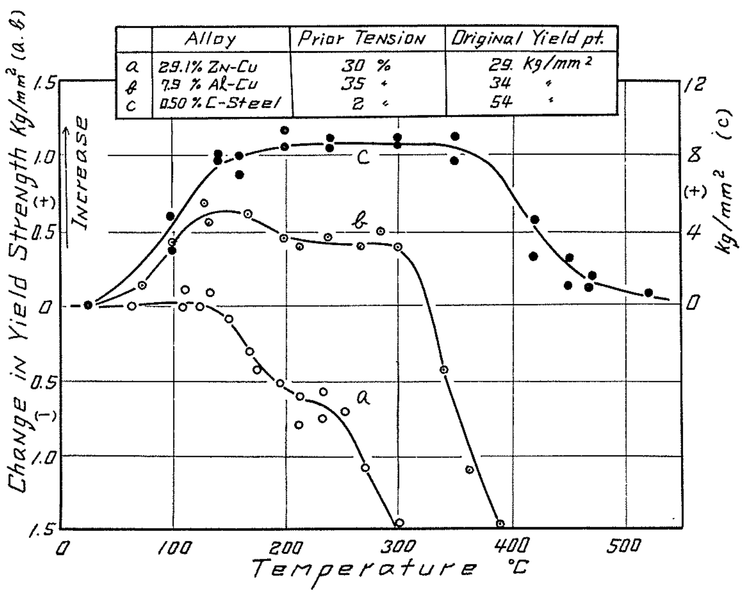


Fig.24 Change of yield strength of extended specimens with annealing temperature.

slight rise within the range of the primary anneal hardening (below 130°C). On the other hand, in carbon steel (curve c), yield point rises greatly within the range of the primary hardening (below 130°C). Hence, it may be considered that the primary hardening of carbon steel can be explained by the mechanisms already proposed, say, of locking of dislocations by solute atoms or of formation of G P zones, while, the anneal hardening of copper alloys can not be explained by adducing such mechanisms. However, in copper alloys yield point is also able to rise only when it is measured under a stress of different sort or different direction from that of prior working, and this rise is probably due to the elimination of Bauschinger effect, unlike in the case of carbon steel.

3. *Bauschinger Effect and Anneal Hardening*

All the theories already postulated with reference to anneal hardening have been on the basis of a rise in yield point. But as described above, it was clarified that the anneal hardening of copper alloys was not accompanied by a rise in yield point under the conditions above mentioned. The anneal hardening seems to be capable of rational explanation by the presumption that its cause is due to elimination of Bauschinger effect. Of course, before the nature of this effect itself stands revealed, the fundamental principle about anneal hardening can not be elucidated, and so it will here be limited to a schematic explanation of anneal hardeinng relying on the presumption above mentioned.

If it is assumed that Bauschinger effect is due to residual stress, the yield point in the working direction would be lowered upon elimination of the effect by low temperature annealing. But in actuality nearly no change was found in the yield point. Therefore, the elimination of the effect is probably due to a change of internal structure, by which anelastic regions gain elasticity.

In Fig. 25, AB' BGCD is the stress-strain curve in the direction of prior working and AECD that in the reverse direction. The curve in any other direction will fall between these two curves. Curve AB′G′CD stands for the mean of the curves in all the directions. If, by low temperature annealing, the curve in the working direction remains unchanged while Bauschinger effect is completely removed, the mean curve after the annealing will come to coincide with that in the working direction, and a hardening corresponding to the area included by the curves B′BGCD and B′G′CD, will be brought about, consequently, the curve in Fig. 23 will show a tendency approximately similar to the anneal hardening curve, and so the higher the degree of prior working, the more pronounced the Bauschinger effect, and moreover, the larger the amount of anneal hardening.

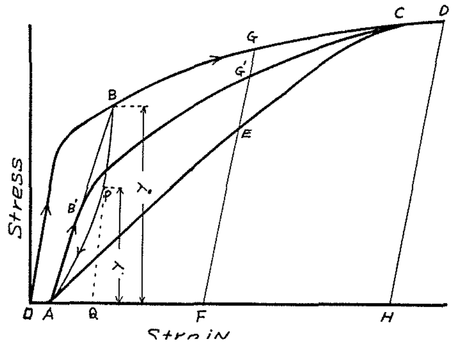


Fig.25 Schematic representation of relation between Bauschinger effect and hardness.

In the case when yield point is measured under a stress different in sort or direction from that of prior working, for instance, when a tensile stress is applied to measure the yield point of a cold rolled specimen of α brass, the yield point is raised by low temperature annealing, as understood by the above explanation.

When hardness is measured by penetrating load, change in hardness by annealing may be different in the case where the load is so small as to produce the small indentation represented by AF in Fig. 25, from that where the load is larger as represented by AH in

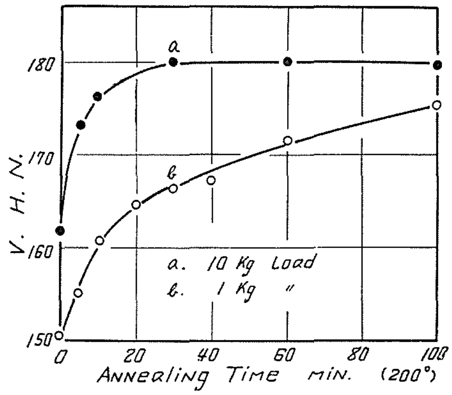


Fig.26 Relation between penetrating load and anneal hardening of 60% rolled specimens of 29.1% Zn-Cu alloy.

the figure. Fig.26 illustrates this difference.

4. *Degree of Cold Work and Anelastic Effect*

From what has been stated on the mechanism of anneal hardening, it may be expected that no critical degree of cold work for anneal hardening can exist, but in fact, as shown in Fig. 27 anneal hardening becomes abruptly pronounced beyond about 15% rolling. This is understood by the gradually widening distance between the curves (a) and (b). The same tendency is also apparent in the case of thermal dilatation (Fig.2) and thermo-E.M.F. (Fig.12).

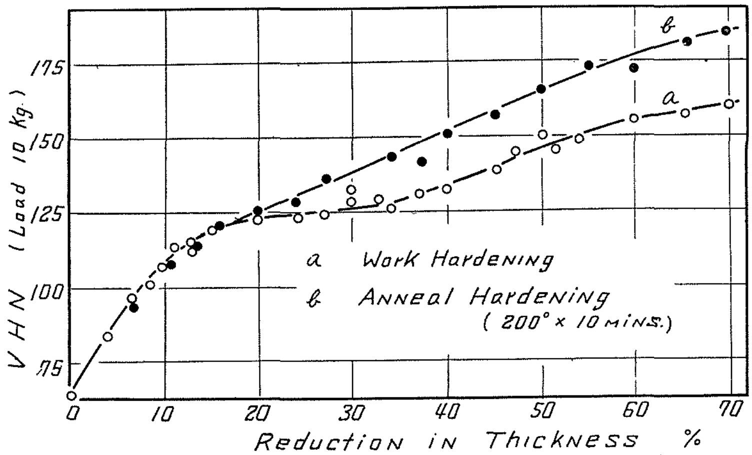


Fig.27 Relation between hardness and rolling reduction of 29.1% Zn-Cu alloy.

For obtaining more exact informations on the subject, anelastic effect in heavily worked specimens was studied. Experiments of Bauschinger effect in the range of high strain are extremely difficult. So, the anelastic deformation being considered to commence upon unloading after prior working at the point P in Fig. 25 where the straight line BP begins to curve, the ratio λ/λ_0 was taken to represnt the degree of anelastic effect. Here, λ and λ_0 are noted in Eig. 25. The ratio is very small in such an alloy as showing little or no anneal hardening. Experiments were made by tension at room temperature (15-21°C).

The results obtained with specimens of Cu-Al alloys and α brass are shown in Fig. 28, which indicates that the ratio increases steeply beyond about 15% strain. It is inferred here that when cold work proceeds to a certain degree, cross slip occurs markedly,[20)21)] causing creation of many vacancies, by which anelastic effect becomes pronounced. As shown by curve (a) in Fig. 27, a stagnation of work hardening[22)] is observed nearly at the same degree of working as above. The stagnation is probably caused by the softening due to this striking anelastic effect. When the anelastic effect is eliminated by low

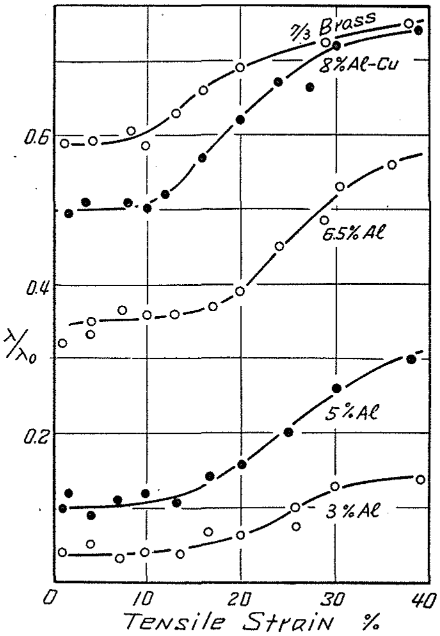


Fig.28 Effect of tensile strain on anelasticity of Cu-Zn and Cu-Al alloys.

temperature annealing, anneal hardening will take place (curve b in Fig.27).

5. *Effect of Concentration of Solute*

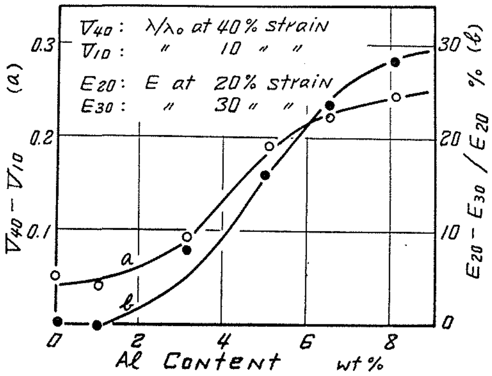


Fig.29 Relation between Al content and elastic and anelastic properties of extended Cu-Al alloys.

By curve (a) in Fig. 29 is shown the relation of Al content in Cu-Al alloys and the ratio λ/λ_0, in which it is evident that the increase of the ratio becomes particularly marked when Al content increases beyond about 3 wt%. This curve shows a tendency similar to that of thermo-E. M. F. (curve a in Fig. 14) and of electric resistance.[23] The fact that a high enough concentration of solute is required for the marked increase, may show that solute atoms in pairs or in the other ordered arrangements assist the occurence of cross slip, that is, the formation of vacancies.

Young's modulus as determined from the straight line AB′B in Fig. 25, shows also the same tendency (curve b in Fig. 29).

6. *Anisotropy in Anelastic Effect*

As will be described in a later section, when in brass the degree of cold work exceeds about 15%, vacancies are produced in large numbers, so that they are easy to form pairs or aggregates, which may have higher mobility. From the extreme smallness of the activation energy for the recovery of internal friction of cold worked α brass at room temperature,[9] it is presumed that migration of vacancies is easy to occur during cold work, and vacancies exhibit an anisotropic arrangement depending on the working condition. Such a non-uniform distribution may enhance an anisotropy in deformation resistnce. Consequently, the deformation resistance in the reverse direction of cold work will be extremely reduced and thus Bauschinger effect becomes marked. When low temperature annealing is then made, vacancies migrate to rearrange isotropically and stabilize or disappear, bringing about higher deformation resistance in the reverse direction. Even at room temperature internal stress appears to cause dispersion and stabilization of vacancies. As the result, hardening (Fig. 9) and recovery of internal friction[9] take place.

7. *Conclusion*

Anelastic effect of α brass and Cu-Al alloys was studied and the following informations were obtained.

(1) As shown in Fig. 24, cold worked α brass does not show a rise in yield point, which was measured after low temperature annealiug under a stress of the same kind and the same direction as that of prior working. This fact, coupled with the occurence of anneal hardening in pure metals also, makes probably it difficult to interpret the anneal hardenig by locking of dislocations by solute atoms or by formation of G P zones.

(2) The above mentioned alloys which reveal marked anneal hardening, show also a pronounced anelastic effect, the elimination of which appears to induce anneal hardening. In other words, a disturbance of the deformation structure, in which lattice defects show an anisotropic arrangement depending on the condition of cold work, is presumed to bring about anneal hardening.

V. Characteristics of Anneal Hardening

As stated in chapt. IV, it may be difficult to accept the interpretation that anneal hardening is due to locking of dislocations by solute atoms or formation of G P zones.[2]

In α brass and Cu-Al alloys, the anelastic effect becomes marked abruptly beyound a certain degree of cold work, and this abrupt change was presumed to be closely related with the generation of vacancies due to cross slip. The generation may result in decrease in density.

Mobility of vacancies during cold work may affect the degree of anisotropy in deformation structure. Therefore, anneal hardening should be greatly dependent on the working conditions such as working temperature. These will here-under be discussed, and furthermore the nature of anneal hardening will be also.

Specimens for these experiments were prepared by the same method as delineated in chapt. II, and low temperature annealing was performed also by the mehod of constant rate heating.

1. *Change in Density*

The method of determining density is based essentially on measuring the volume of water being identical to that of the specimen to be studied.

(1) Degree of cold work and density

Curve (a) in Fig. 30 shows the relation of degree of drawing versus density of 8.1% Al-Cu alloy. When the degree exceeds about 10%, density drops suddenly, its tendency showing the same as that of anneal hardening (Fig. 27), thermo-E. M. F. (Fig. 12) and electric resistance.[24] This confirms the presumption that vacancies are created in large numbers beyond a certain degree of cold work.

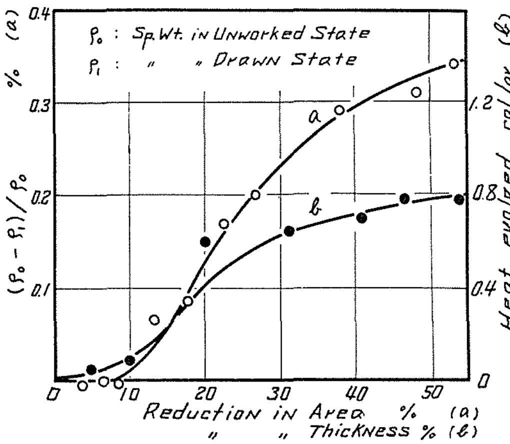


Fig 30 (a) 8.1% Al-Cu, Density vs. degree of drawing.
(b) 30.8% Zn-Cu, Thermal change vs. degree of compression.

The same applies also to the increase in internal energy, as shown by curve (b) in Fig. 30. Here, the amount of thermal change was obtained from the change of heat evolution in the temperature range near 160°C by finding the area included between the specific heat-temperature curves of uncompressed and compressed specimens of α brass. Measurements of specific heat were made by Sykes's method.

(2) Concentration of solute and density

In Fig. 31 is shown the relation of the decrease in density by drawing versus Al content of Cu-Al alloys. Decrease in density becomes prominent when Al content exceeds about 3 wt%. It shows that a high enough concentration of solute is required, in the copper alloys, for the easy occurence of cross slip, which creates vacancies. The dependency of density on the concentration is conformable to that of λ/λ_0 (Fig. 29), indicating that the generation of vacancies is the main cause of the anelastic effect above stated.

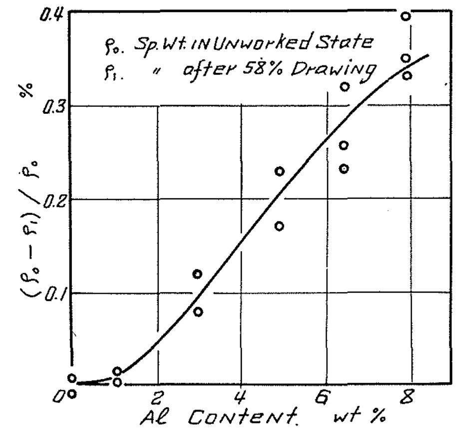


Fig.31 Effect of Al content on change in density of Cu-Al alloys

The curve in Fig. 31 shows also the same trend as that of thermo-E. M. F.

(curve a in Fig. 14) and electric resistance.[14] Increase in electric resistance due to cold work has been accepted to be mainly attributed to the formation of vacancies, and the results in Figs. 30 and 31 prove this consideration. Accordingly, it is probably evident that the changes in the various properties of the copper alloys on heating after cold work are introduced chiefly by the change in the number and in the arrangement of vacancies.

(3) Temperature dependency of density

The change of density with annealing temperature. as shown in Fig. 5, is rather widely different in trend from that of thermo-E.M.F.(Fig.16). Here, it may be supposed that the dissimilarity is only apparent, for the experimental accuracy was lower in density than in thermo-E. M. F., preventing a closer similarity of the curves to come forth. Within the temperature ranges of anneal hardening, both these properties recover about 60% of their amounts changed by cold work. By heating after cold work, vacancies in the state of pair or aggregate migrate to stabilize or partly disappear. In anneal hardened state, about 40% of the vacancies created by cold work remain uneliminated, and these cause a variety of complicated secular changes thereafter.

2. *Temperature of Cold Work and Anneal Hardening*

(1) Temperature of tension and anelastic effect

By the same method as stated concerning Fig. 23, the ratio λ/λ_0 was measured at various temperatures. The results are shown in Fig. 32. The degree of cold work at which the ratio increases abruptly, is the larger the lower the working temperature, indicating that cross slip is difficult to occur at low temperatures.

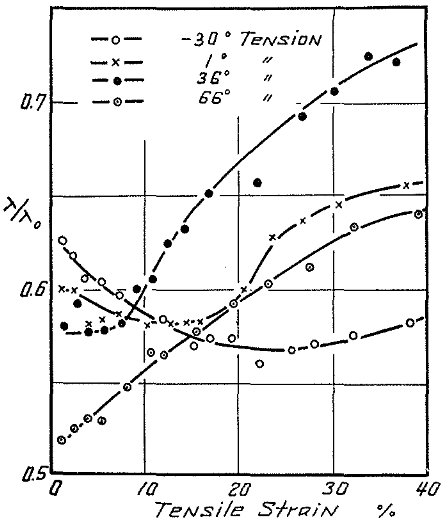


Fig.32 Effect of working temperature on anelasticity of 29.0% Zn-Cu alloy.

(2) Temperature of rolling and anneal hardening

On the relation of rolling temperature and anneal hardening, there has been a report,[25] but as the effect of rolling degree on this relation has not fully been elucidated, attempts were made for this purpose. The results are given in Fig.33. Here, degree of anneal hardening was obtained from the as-worked hardness and the maximum hardness in the hardness-annealing temperature curve. The results show a trend similar to that in Fig. 32. In the later stages of deformation, there is little effect of working

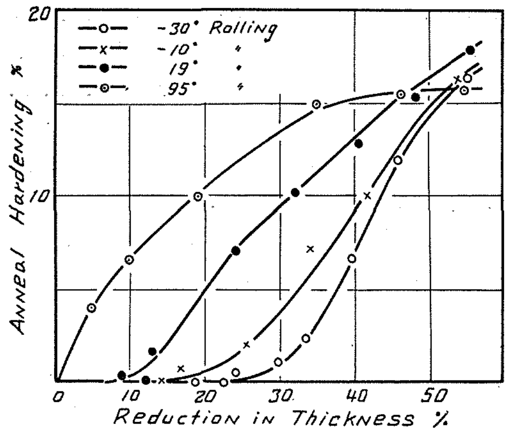


Fig.33 Effect of rolling temperature on anneal hardening of 29.0% Zn-Cu alloy.

temperature, but in the earlier stages, anneal hardening is the more marked the higher the temperature.

The facts that the ratio λ/λ_0 and the degree of anneal hardening are greatly dependent on working temperature, may show that a diffusion takes place during cold work. Therefore, the activation energy for the diffusion is considered to be very small, and in α brass probably of a value nearly equal to the value $<10{,}000$ cal/mol cbtained from the recovery of internal friction after cold work.[9]

3. *Behavior of Vacancies and Anneal Hardening*

It may be evident from what has been stated above that a diffusion is easy to occur during cold work in such alloys as showing marked anneal hardening. As already reported,[26)27)] vacancies may induce softening, and it is inferred that the mobility of vacancies would affect the strength of materials, and hence, that the cause of anneal hardening is due to the stabilization of vacancies, which are arranged in an anisotropic manner by cold work. With reference to the stabilization, the influence of dislocations must be taken into account, but on this later on.

Since diffusion is probably easy to occur during cold work, vacancies show the anisotropic arrangement depending on the working condition, that is, they are apt to aggregate on particular planes or sites. This segregation is considered to cause back stress and thus an anisotropic anelasticity. When some kind of stimulaiton is applied to derange the arrangement, such anisotropic viscous regions may disappear and the strength becomes isotropic.

4. *Two Stages Annel Hardening*

As stimuli causing derangement of the deformation structure, internal stress and thermal diffusion may be cited. The former seems to induce room temperature hardening (Fig. 9) and the primary anneal hardening observed below 130°C (Fig. 1 and 2). The vacancies created in large numbers during cold work may readily form pairs or aggregates, and in addition, they are presumed to easily migrate even under low internal stresses. The above presumption may be acceptable by the reason that the activation energy for the migration may be very small, probably of a value $<$ 10,000cal/mol.[9] Since some of vacancies disappear during migration, electric resistance and thermo-E. M. F. decrease.

The above hardening is caused by internal stress, while the secondary hardening (150-250°C) may be induced by thermal diffusion. The activation energy for the latter is about 20,000 cal/mol in α brass[28] — a value clearly representing the energy of thermal diffusion of solute atoms.

5. *Working Condition and Anneal Hardening*

Anneal hardening is greatly dependent not only on the working temperature but also on the other conditions of cold work.

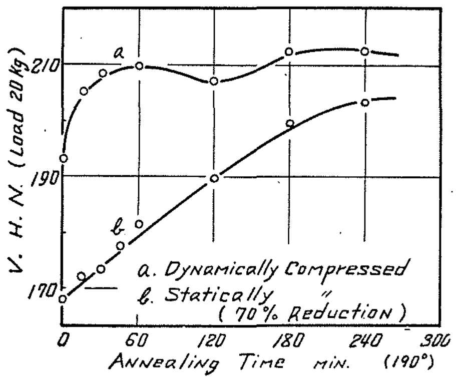


Fig.34 Effect of rate of compression on anneal hardening of 31.3% Zn-Cu alloy.

In Fig. 34 is shown the effect of rate of cold work. A statically compressed specimen shows less work hardening and more anneal hardening than that impactly compressed. It is probable that the higher the rate of cold work, the less marked the diffusion of vacancies. The generation of heat upon impact working may be adduced as having some effect, but the results of measurements showed that the rise in temperature thereby did not exceed about 40°C in the maximum, so that the effect of heat generation may be fairly disregarded.

When plastic plates of tetra-fluoro ethylene with low coefficient of friction are inserted upon rolling between the rollers and the specimen to be rolled, the anneal hardening is less marked than in the case when the friction is large. It may generally be said from the experimental results that the more the friction above stated, or the more complex the stress of cold work, the more the generation of vacancies, that is, drawing rather than rolling or compression, or cross rolling rather than straight rolling is found to entail more marked anneal hardening. Also in pure copper, cross rolling has been reported to show less work hardening.[29]

6. *Solute Atoms and Anneal Hardening*

In Fig. 35 are shown the anneal hardening curves of various Cu-Al alloys. The higher the concentration of solute, the more marked the anneal hardening. The trend of the concentration dependency (curve c in Fig. 14) is the same as

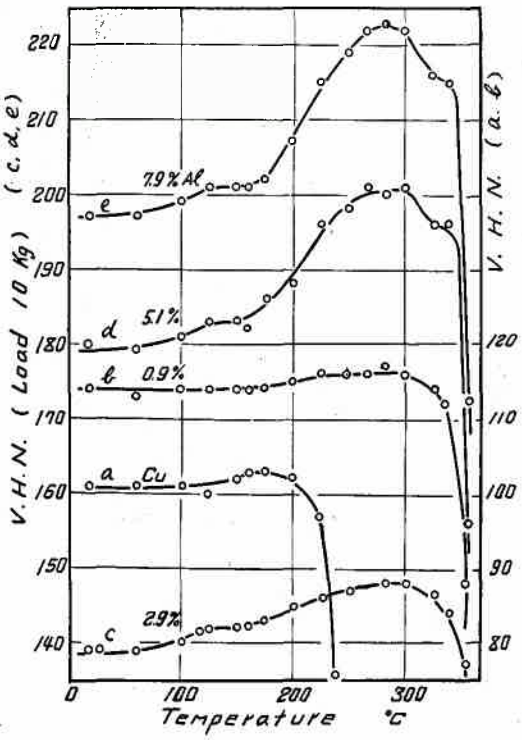


Fig.35 Anneal hardening curves of Cu-Al alloys rolled to 70% reduction.

that of various physical properties already stated. This may lead to the presumption that solute atoms differing in size from solvent atoms partake in the deformafion in the state of pairs or the other ordered arrangements, helping generation of vacancies and formation of an anisotropic deformation structure. At low solute concentrations, most solute atoms are far apart and the chance of forming such ordered arrangements is quite small.

7. *Micro-Structure*

When cold worked specimens of α brass and Cu-Al alloys are electro-polished and then etched with $FeCl_3$ solution, strain marking as shown in Fig. 36 can be observed. In 0~3% Al-Cu alloys, such

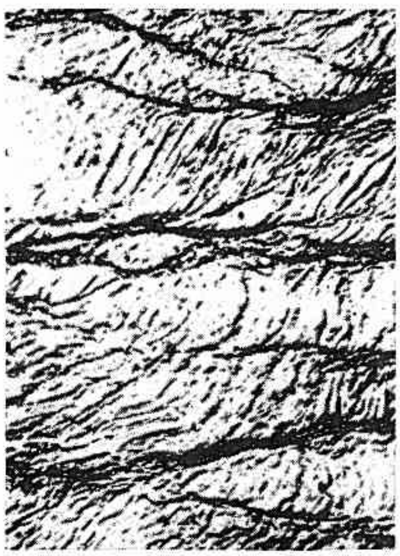
↓   ↑

Fig. 36-1 Microstructures of 8.1% Al-Cu alloy 39% drawn (a) and 29.0% Zn-Cu alloy 60% rolled. ×600

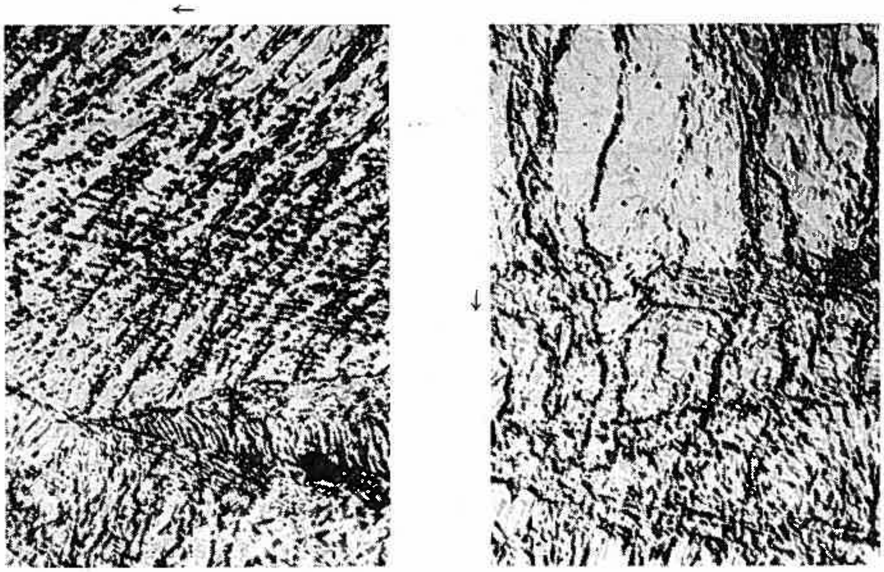


Fig.36-2 Microstructures of 29.0% Zn-Cu alloy 60% rolled and subsequently annealed at 220°C (a) and 280°C (b) ×600
(Arrow indicates work direction.)

lines could hardly be detected even after severe working. It may, therefore, be presumed that the lines are produced owing to the non-uniform distribution of concentration such as segregation of vacancies and solute atoms rather than pile-up of dislocations.

Examinations on such lines revealed the followings.

(1) Upon rolling at room temperature, the lines begin to appear when the degree increases beyond about 15% reduction, while, at 100°C they are detected even in the earlier stages of deformation.

(2) In Cu-Al alloys, the lines can hardly be observed in the case when Al content is less than about 3 wt%.

(3) When low temperature annealing is made, the lines tend to become fragmentary.

(4) Their arrangement becomes anisotropic as deformation proceeds and in the case of rolling, they arrange at roll surface in the direction perpendicular to rolling.

These findings show the same trend as the changes in the various properties already stated.

8. *Grain Size and Anneal Hardening*

Generation of vacancies during cold work is probably easy to occur at or in the neighborhood of grain boundaries, and in accordance, it is closely dependent on their shape and size. Anneal hardening is more marked at grain boundaries than within grains.[30]

The above mentioned line observed in the micro-structures, can be detected only in the vicinity of grain boundaries in the earlier stages of deformation. With heavier working, these lines increase in the number and a fragmentation occurs. Hence, anneal hardening may arise even in single crystals quite as in polycrystals, if the working is severe.

9. *Pure Metals and Other Alloys*

Pure metals quite as brass, may be expected to show anneal hardening, if an anisotropically anelastic effect is induced by cold work. Since, however, the anelastic effect due to cold work is not generally cospicuous in pure matals the anneal hardening is less marked.

The fact that anneal hardening is also observed in Cu-Ni alloys, which indicate solid solutions in all proportions, may show that the theory of anneal hardening on the basis of a change in solubility limit by cold work, is not acceptable. In the case of alloys consisting of more than one phase, the anelastic effect being marked in the vicinity of boundaries of the phases anneal hardening can also be observed, but on this on a later occasion.

10. *Conclusion*

Study on the characteristics of anneal hardening was chiefly carried out and the results obtained are as follows.

(1) Anneal hardening is greatly dependent on working temperature, suggesting that diffusion easily takes place during cold work in such alloy as showing marked anneal hardening. Exceptionally high ductility of α brass is probably attributable to this diffusion.

(2) During cold work, an anisotropic structure is formed by segregation due to the diffusion of vacancies. It may be inferred that this structure is readily subjected to an anisotropic viscous flow, and when the arrangement of vacancies in the structure is disturbed, the viscous regions are disintegrated, causing anneal hardening. As stmuli occasioning such a derangement, internal stress and thermal diffusion may be enumerated. Besides, mechanical treatment can also be cited, so that a hardening similar to anneal hardening can be expected to occur by deformation without low temperature annealing, as reported later on.

VI. Some Phenomena Related with Anneal Hardening

In chapt. V above, it was proposed that anneal hardening was mainly caused by migration and dispersion of anisotropically arranged vacancies. For elucidating the fundamental principle of anneal hardening, it is thus requisite first to study extensively the behavior of vacancies. However, the mutual interaction between the vacancies and the dislocations which govern the behavior of vacancies and its temperature dependency in severely worked specimens are complicated matters. While, since anneal hardening is attended by such anomalous phenomena as retrogression effect, work softening [15] and anomalous softening [25] etc., the author wish first to make the principle of anneal hardening more definite by studying these attendant phenomena, hereunder.

Specimens were obtained by the same method as described in chapt. II above, and the same constant rate heating method as above was adopted for low temperature annealing.

1. *Retrogression Effect*

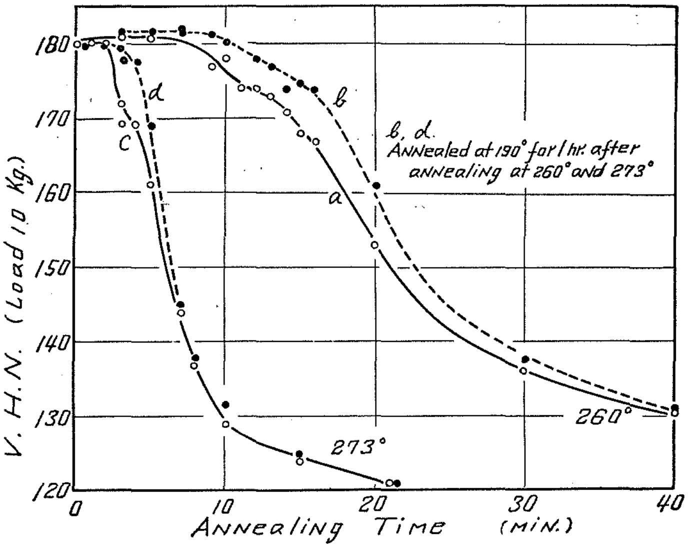


Fig.37 Change in hardness with annealing time of 28.4% Zn-Cu alloy rolled to 65% reduction and annealed at 190°C for 90 mins.

In Fig. 37, curves (a) and (c) represent hardness - annealing time curves on annealing at 260°C and 270°C of anneal hardened specimens of α brass, respectively. The second of the two stages softening in the curves is due to recrystallization, and the primary is of the same kind as the softening shown in the hardness - temperature curve (curve d in Fig. 3) as observable just after the secondary anneal hardening. When specimens were annealed at the temperatures indicated in the figure for the duration shown in the abscissa there and then re-annealed at 190°C for 1 hour (as in curves b and d), anneal hardening was observed again, provided that the recrystallization has not progressed too far. That is to say, an effect similar to the retrogression effect in age hardenable Al alloys can be observed in the case of anneal hardening also. It is, however, inappropriate to explain anneal hardening by the same mechanism as that of age hardening.

This retrogression effect may be interpreted as follows. This softening accompanies a slight increase in thermo-E.M.F. (as shown in the range 220°~260°C in Fig. 16). Since polygonization or formation of recrystallization nuclei is considered to occur in this temperature range, vacancies are probably created thermally in a few numbers, and there may be a change in mutual interaction ameng lattice defects. It is these changes that bring about the softening, so that reannealing at a low temperature would result in anneal hardening. Vacancies seem to show again the anisotropic arrangement depending on working conditions by retrogression treatment, for such a retrogression effect can also be observed in the change in thermal dilatation (Fig. 11). Since, however, during retrogression treatment the disappearance of vacancies and the recrystallization as the process of recovery go on without rest, the retrogression effect becomes less marked, when retrogression treatment and low temperature annealing are repeated

Since a softening (Fig. 3) and a slight increase in thermo-E. M. F. (Fig. 16) can also be observed just after the primary anneal hardening at 100~150°C, it is probable that vacancies are also created.

2. *Work Softening*

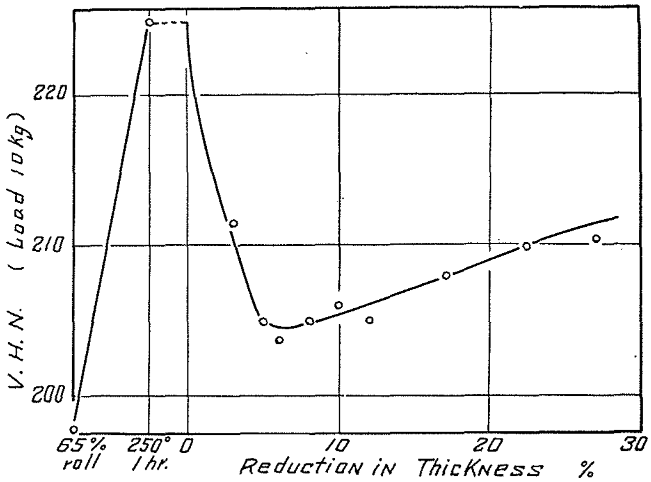


Fig.38 Relation between hardness and degree of rolling of anneal hardened 7.9% Al-Cu alloy.

In Fig. 38 is revealed the work softening of Cu-Al alloy. When a slight working of the same mode as that of the prior working is applied secondarily after anneal hardening, softening occurs. Since a silght application of the secondary working induces only a little increase in thermo-E.M.F. (Fig. 19), formation of vacancies must be petty. It may, therefore, be considered that by such a slight application, an anneal hardened specimen is forced to come back in the state before low temperature annealing, and as the result softening occurs.

As given in Fig. 39, Bauschinger effect becomes again marked by a slight secondary working. Namely, when low temperature annealing is made after the prior torsion, Bauschinger effect is removed (curve a), but when a specimen is slightly re-twisted in the direction of prior torsion after low temperature annealing under zero load, the effect becomes again pronounced (curve b).

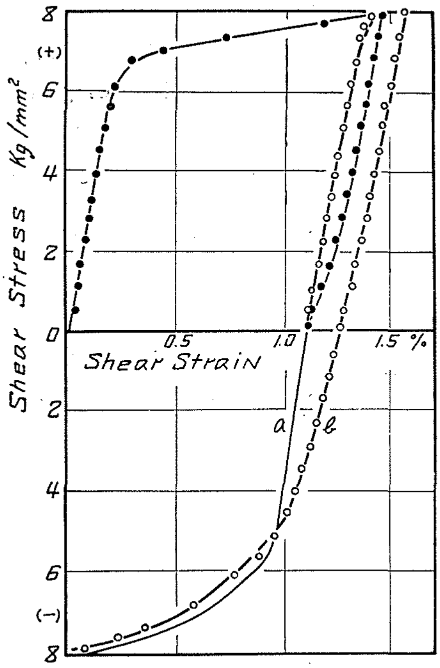


Fig.39 Torsion stress-strain diagram of 33.2% Zn-Cu alloy.

In Fig.40 are shown the rolling degree-hardness curves of severely drawn specimens of various Cu-Al alloys. With the progress of such a different mode-secondary working, the specimens first hardened and then softened. This hardening will be called "secondary work hardening" here-under. The degree of this hardening [$(H_1-H_0)/H_0$] has been given by curve (b) in Fig. 14. Secondary work hardening becomes also marked when Al content in Cu-Al alloys is beyond about 3 wt%. α brass shows a similar hardening (curve a in Fig.41).

The secondary work hardening seems to have little or no relation with disappearance of vacancies, an isotropic structure is obtained by low temperature annealing, its stability is weak. Therefore, it is probable that vacancies are very sensitive to temperature and in addition, they are easily dispersed and activated under very low stresses. Thus, activation of vacancies may be taken place also by internal stress, by which complicated secular changes after anneal hardening are thought to occur.

3. *Secondary Work Hardening*

When a secondary working differing from the primary in mode is appiled, the results are more complex than in the case when the both workings are the same in mode.

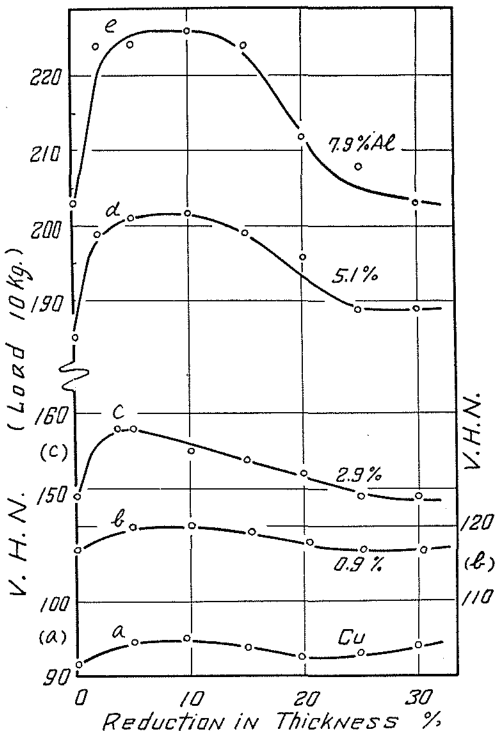


Fig.40 Relation between hardness and degree of rolling of Cu-Al alloys drawn to 64% reduction.

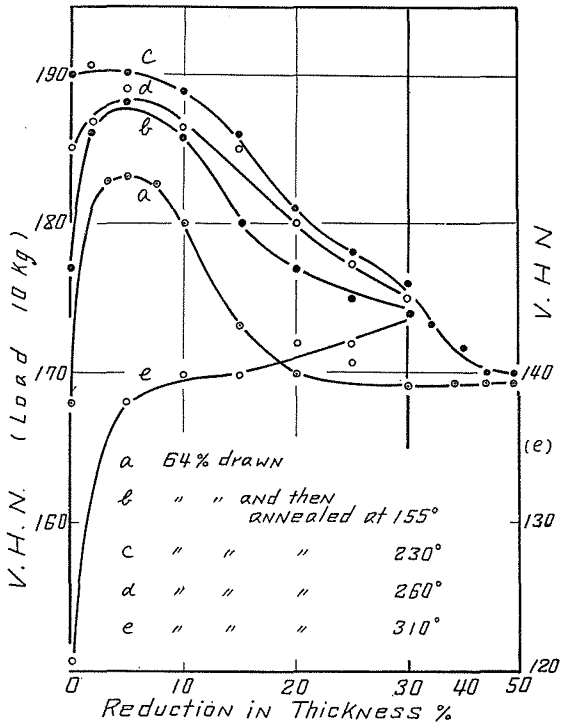


Fig.41 Relation between hardness and degree of rolling of 29.1% Zn-Cu alloy drawn to 64% reduction, and subsequently annealed at the illustrated temperatures.

since no change in thermo-E.M.F. is found accompanying it (Fig. 18). It is presumed that a forced diffusion due to the different mode-secondary working, results in destruction of the as-primary-worked structure and induces this secondary work hardening. In the case when the primary working is made by rolling and the secondary by compression, secondary work hardening can also be observed.

It is not that the destruction of the as-primary-worked-structure by a different mode-secondary working always induces secondary work hardening, but in some cases the different mode-secondary working will promote an anisotropically anelastic effect, and brings abouts softening.[31] The modes of cold work, in the descending order of the magnitude of degree of anneal hardening, are as follows:

(1) Drawing, (2) Rolling, (3) Compression, (4) Tension.

When the secondary working is of a mode lower in the above order than the primary working, secondary work hardening will appear, but when vice versa, softening occurs in some cases.

4. *Secondary Work Hardening and Anneal Hardening*

When low temperature annealing is made before different mode-secondary working, the amount of secondary work hardening is reduced (Fig.41). Curve (a) in Fig. 42 represents the change in the degree of this hardening with annealing temperature, as expressed by the ratio $(H_1-H_0)/H_0$, where H_0 is the hardness of specimens annealed at the temperature indicated on the abscissa after the primary drawing, and H_1 the hardness of the same subjected to secondary working of 5 % rolling after this anneal treatment. With the progress of anneal hardening, the degree of secondary work hardening is lowered in two stages.

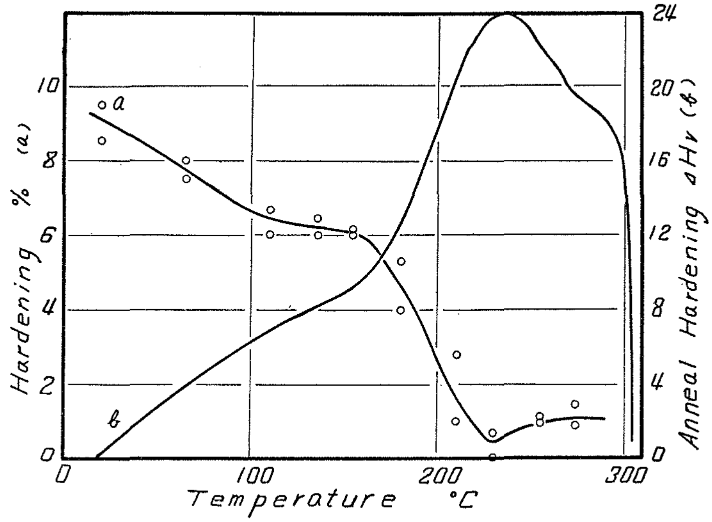


Fig.42 Hardening curves of 29.1% Zn-Cu alloy drawn to 64% reduction.

(a) Hardening curve by rolling to 5～8% reduction after drawing and subsequent annealing at the temperature shown on the abscissa.

(b) Anneal hardening curve.

It may be inferred from the above results that anneal hardening and secondary work hardening are induced by nearly the same cause, and therefore that anneal hardening is obtained not only by annealing but also by different mode-secondary working. That is, anneal hardening and secondary work hardenig are similar phenomena due to destruction of the deformation structure. They are dissimilar only in that in the former, the destruction is caused by internal stress and thermal diffusion, while in the latter, it is caused by forced diffusion due to cold work.

5. *Softening after Secondary Work Hardening*

On continued working after secondary work hardening, softening occurs. In α brass as shown by curve (a) in Fig. 41, the softening is observed in the range of 5～20% of rolling.

Destruction of the as-primary-worked structure, in which lattice defects exhibit an anisotropic arrangement, induces the secondary work hardening, and with the progress of different mode-secondary working, the destructed structure transforms gradually to the structure specific to the secondary working, so that the anisotropic arrangement is again brought about, causing softening. Difference in the mode of cold work results in difference in the arrangement but also in the number of vacancies, and upon transition of drawn structure into rolled structure some vacancies are removed and thermo-E.M.F. is reduced (Fig.18).

When an anisotropic deformation structure is brought about the hardness falls, but once deranged by some stimuli, the hardness rises. As given in Fig. 43, in the case of 5% reduction of secondary rolling, the hardness is high (curve c), but the structure specific to drawing (curve a) or rolling (curve b) is obtained, the hardness becomes small. When the deformation structure is uniformly destroyed by low temperature annealing, all the specimens show nearly the same hardness.

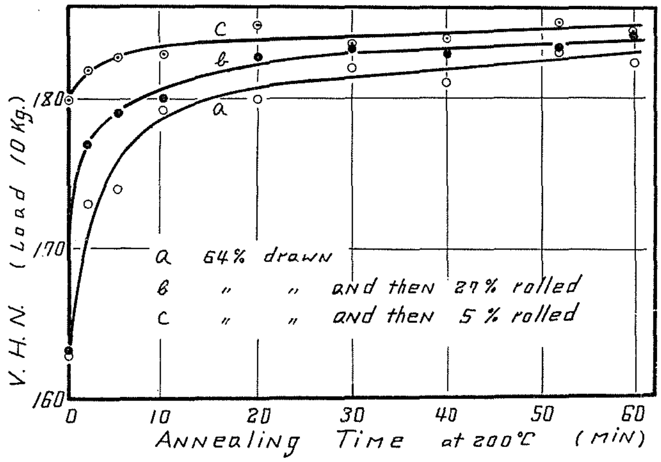


Fig.43 Change in hardness with annealing time of 29.1% Zn-Cu alloy.

It may be inferred from the above results that the cold worked specimens are in the softened state by the anisotropically anelastic effect, and when such a cause of softening is removed by low temperature annealing, the work hardened state merely dependent on dislocations can be obtained.

6. *Secular Change*

It can be inferred from several relevant phenomena that the behavior of vacancies and the mutual interaction of vacancies and dislocations, are greatly dependent on temperature. The structure stabilized by low temperature annealing is not necessarily stable at room temperature. When an anneal hardened specimen is aged at room temperature, a secular change is brought about, probably by a re-activation of numerously retained vacancies. The factors causing such a re-activation may be sought in internal stress and temperature dependency of the mutual interaction of lattice defects. Anomalous softeing[25] also may be attributed to the same factors.

VII. General Summary

Amongst theories already proposed for explaning anneal hardening, those of locking of dislocations by solute atoms and formation of G P zones, have recntly been under consideration, but all these seem to be hardly acceptable by the following reasons.

(1) As described with reference to Fig. 24, no rise of yield point corresponding to the anneal hardening could be detected upon measuring under a stress the same in kind and direction as that of prior working. Therefore, a theory being merely on the basis of a rise in yield point may not be capable of explaining anneal hardening.

(2) Anneal hardening can also be observed in pure metals. Judging from the similarity of the characteristics of anneal hardening of the copper alloys and pure metals, it may hardly be addmitted that the anneal hardening of the copper alloys is different in its nature from that of pure metals.

(3) Anneal hardening is brought about not only by low temperature annealing, but also by a mechanical treatment.

The conclusion obtained in this study with reference to α brass and Cu-Al alloys is as follows. In such copper alloys, vacancies are created in large numbers during cold work and form pairs or aggregates, which have higher mobility. Such vacancies migrate during cold work to show anisotropic arrangement and shape depending on working condition, causing back stress originated in internal stress of the aggregates and hence a marked anelastic effect to appear in the material. Such a structure, once destroyed by some stimuli, will have its anelastic effect eliminated, and hardening sets in. This hardening is anneal hardening, and it is caused by internal stress and thermal diffusion, and in addition by forced diffusion due to cold work, of vacancies.

Anisotropic anelasticity and anneal hardening, as given in Figs. 32 and 33 respectively, are both greatly dependent on working temperature, probably showing that diffusion occurs during cold work. The activation energy for the diffusion during cold work seems to be very small, on the presumption of the magnitude of activation energy for the recovery of internal friction of cold worked α brass.[9] The diffusion, in accordance, is considered to be very easy to occur during cold work in such materials as showing conspicuous anneal hardening. The diffusion results in an anisotropic arrangement of vacancies, and so extremely anisotropic viscous regions, which is considered to bring about a softening of material.

Mutual interactions between solute atoms, vacancies and dislocations, and their temperature dependency in a severely cold worked material, are complicated matters, and further researches on the subject will be awaited. Besides, studies must also be expanded on the effect of crystal orientation or crystal plane.

In conclusion, the author expresses his cordial thanks to Dr. T. Sato, professor of the Tohoku University, under whose kind direction the present investgation was carried out. His thanks are also due to the menbers of the Subcomittee for Anomalies in Solid Solution of Copper Alloys of the Japan Institute of Metals, for their helpful discussions and suggestions, and to K. Takahashi for his zealous assistance.

(Received September 24,1958)

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山形大学紀要（工学）第5巻　第2号

銅合金の焼鈍硬化に関する研究

西　野　知　良

工 学 部 機 械 工 学 科

炭素鋼の歪時効硬化に類似の現象が銅合金にもあり，焼鈍硬化と呼ばれている。この現象は溶質原子による転位の固着又は G P 帯の生成等の機構で説明されているが，種々の矛盾を含んでいる。

この現象は低温焼鈍によって得られるのであるが，その他にも機械的に変形加工しても得られるのである。即ち，塑性加工の条件に依存する加工組織が破壊されて得られる硬化であり，必ずしも低温焼鈍を必要としない。

或る限度以上に溶質原子を含む α 黄銅及び Cu-Al 合金は冷間加工中に原子又は格子欠陥の拡散が起り易く，それらが異方的に配列又は偏析して，その相互干渉により特殊の粘性領域を作る。即ち冷間加工すると軟化した状態にあり，その組織がある刺戟によって乱されると，焼鈍硬化が起ると解釈される。